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<b>(54) Title:</b> HYDROPHOBIC SILICA GELS WITH REDUCED SURFACE AREA  <b>(57) Abstract</b>  <p>The present invention is hydrophobic silica gels having reduced surface area and a method for their preparation. The method comprises three steps, where in the first step a mixture comprising a silica hydrosol and colloidal silica is formed. In the second step the mixture is heat treated in the presence of a strong mineral acid at a pH less than about 1 to form a silica hydrogel having incorporated therein colloidal silica. In the third step the silica hydrogel is contacted with an organosilicon compound in the presence of a catalytic amount of a strong acid to effect hydrophobing of the silica hydrogel thereby forming a hydrophobic silica gel having a surface area within a range of about 100 m<sup>2</sup>/g to 450 m<sup>2</sup>/g as measured in the dry state. In a preferred method the hydrophobic silica gel is contacted with a sufficient quantity of an organic solvent immiscible with water to convert the hydrophobic silica hydrogel into a hydrophobic silica organogel.</p>		

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## HYDROPHOBIC SILICA GELS WITH REDUCED SURFACE AREA

### BACKGROUND OF INVENTION

The present invention is hydrophobic silica gels having reduced surface area and a method for their preparation. The method comprises three steps, where in the first step a mixture comprising a silica hydrosol and a colloidal silica is formed. In the second step, the mixture is heat treated in the presence of a strong mineral acid at a pH less than about 1 to form a silica hydrogel having incorporated therein colloidal silica. In the third step the silica hydrogel is contacted with an organosilicon compound in the presence of a catalytic amount of a strong acid to effect hydrophobing of the silica hydrogel thereby forming a hydrophobic silica gel having a surface area within a range of about 100 m<sup>2</sup>/g to 450 m<sup>2</sup>/g as measured in the dry state. In a preferred process the hydrophobic silica gel is contacted with a sufficient quantity of a water-immiscible organic solvent to convert the hydrophobic silica hydrogel into a hydrophobic silica organogel. The organic solvent can then be removed from the organogel to form a hydrophobic silica gel having a surface area within a range of about 100 m<sup>2</sup>/g to 450 m<sup>2</sup>/g as measured in the dry state. A water soluble compound of cerium or iron may be added in the second step to improve the heat stability of the hydrophobic silica gel.

Although hydrophobic silica gels prepared by the present method are useful in many applications such as thermal insulating, reinforcing and extending filler in natural rubbers, and as filler in floatation devices, they are particularly useful as reinforcing fillers in silicone rubber compositions. It is well known that silicone rubber formed from the vulcanization of polydiorganosiloxane fluids or gums alone generally have low elongation and tensile strength values. One means for improving the physical properties of such silicone rubber involves the incorporation of a reinforcing silica filler into the fluid or gum prior to curing. However, silica reinforcing fillers have a tendency to interact with the polydiorganosiloxane fluid or gum causing a phenomenon typically referred to as "crepe hardening." A great deal of effort has been made in the past to treat the surface of reinforcing silica fillers with organosilanes or organosiloxanes to make the surface of the silica hydrophobic. This surface treatment reduces or diminishes the tendency of the

compositions to crepe harden and improves the physical properties of the cured silicone rubber.

Brown, U. S. Pat. No. 3,024,126, teaches a method for making a pre-formed reinforcing silica filler hydrophobic by treating it in an organic solvent with an  
5 organosilicon compound, such as an organosilane or low-molecular weight organosiloxane containing 0.1 to 2 total hydroxyl and/or alkoxy radicals per silicon atom, and a small amount of amine, quaternary ammonium, or organometallic compound.

Lewis, U. S. Pat. No. 3,979,546, teaches a method for making the surface of reinforcing silica fillers hydrophobic through the use of alpha-alkoxy-omega-siloxanols  
10 with alcohols under mild conditions. The fillers taught are pre-formed solids.

Tyler, U. S. Pat. No. 3,015,645, teaches the making of hydrophobic silica powders by reacting an organosilicon compound such as dimethyldichlorosilane or trimethylmethoxysilane with a silica organogel in the presence of an acidic catalyst and then removing the volatile materials. The method requires the preparation of a silica hydrogel  
15 which is converted to a silica organogel by replacing the water in the hydrogel with an organic solvent.

Lentz, U. S. Pat. No. 3,122,520, teaches a procedure where an acidic silica hydrosol is first heated to develop a reinforcing silica structure and then mixed with an organosilicon compound, an acid catalyst, and a water-immiscible organic solvent to produce a  
20 hydrophobic silica filler. The organosilicon compounds taught by Lentz are limited to those compounds in which the organic radicals bonded to silicon atoms have less than 6 carbon atoms, organosilicon compounds having no organofunctional substituents bonded to silicon atoms, and to organosilicon compounds having no hydrogen bonded to silicon atoms.

Alexander et al., U. S. Pat. No. 2,892,797, describe silica sols modified by treatment  
25 with a solution of a metalate so that the silica particles are coated with no more than a molecular layer of a combined metal which forms an insoluble silicate at a pH between 5 and 12. Aluminum, tin, zinc, and lead are taught as the preferred metals. Alexander et al. teach that silica sols which carry a metal upon the surface of the particles according to their invention have increased stability at pH extremes.

Termin et al., U. S. Pat. No. 3,850,971, and Termin et al. U. S. Pat. No. 4,006,175  
30 teach that porous silicic acid having a specific surface area of about 50 m<sup>2</sup>/g to 1000 m<sup>2</sup>/g

can be made by hydrolyzing methyl or ethyl silicate or polymethyl or polyethyl silicate with about 70 to 120% of the stoichiometric amount of water with moderate stirring. Termin et al. teach that transition metals such as iron oxides and chromium oxides may be used as hydrolysis activators and that such metals may appear in the end product.

5 Nauroth et al., U. S. Pat. No. 4,360,388, teach cerium containing precipitated silica. Nauroth et al. teach that silicone rubber compositions reinforced with the cerium containing precipitated silica exhibit excellent heat stability and that the cerium containing precipitated silica acts as a fire retardant agent.

Nauroth et al., U. S. Pat. No. 4,208,316, teach the use of hydrophobic precipitated  
10 silica as a reinforcing filler in plastic masses which are hardenable to form elastomers.  
Such elastomers include silicone elastomers.

The hydrophobic silica gels prepared by the present method have improved compatibility with polydiorganosiloxane polymers, when compared to silica gels prepared in the absence of the colloidal silica. Therefore, the present hydrophobic silica gels incorporating the colloidal silica are especially suited for use as reinforcing fillers in compositions curable to form silicone rubber. Such cured compositions can have improved physical properties such as tear and tensile strength, when compared to compositions using hydrophobic silica gels as reinforcing filler without the incorporation of colloidal silica.

## 20 SUMMARY OF INVENTION

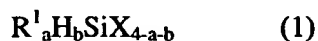
The present invention is hydrophobic silica gels having reduced surface area and a method for their preparation. The method comprises three steps, where in the first step a mixture comprising a silica hydrosol and colloidal silica is formed. In the second step, the mixture is heat treated in the presence of a strong mineral acid at a pH less than about 1 to form a silica hydrogel having incorporated therein colloidal silica. In the third step the silica hydrogel is contacted with an organosilicon compound in the presence of a catalytic amount of a strong acid to effect hydrophobing of the silica hydrogel thereby forming a hydrophobic silica gel having a surface area within a range of about 100 m<sup>2</sup>/g to 450 m<sup>2</sup>/g as measured in the dry state. In a preferred method the hydrophobic silica gel is contacted with a sufficient quantity of an organic solvent immiscible with water to convert the hydrophobic silica hydrogel into a hydrophobic silica organogel. The organic solvent can

be removed from the hydrophobic silica organogel to form a hydrophobic silica gel having a surface area within a range of about 100 m<sup>2</sup>/g to 450 m<sup>2</sup>/g as measured in the dry state.

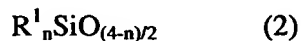
### DESCRIPTION OF INVENTION

5 The present invention is hydrophobic silica gels having reduced surface area and a method for their preparation. The method for preparing the hydrophobic silica gels comprises:

- (A) forming a mixture comprising (i) a silica hydrosol comprising about 0.02 g to 0.5 g of SiO<sub>2</sub> per milliliter and having an average particle size less than 4 nm and (ii) about 0.1 to 10 50 weight percent of colloidal silica having an average particle size of at least 4 nm, (B) heating the mixture in the presence of a strong mineral acid at a pH less than about 1 and a temperature within a range of about 20°C to 250°C to form a silica hydrogel having the colloidal silica incorporated therein, and (B) contacting the silica hydrogel with (1) a catalytic amount of a strong acid in an amount 15 sufficient to effect reaction of (2) an organosilicon compound selected from the group consisting of organosilanes described by formula



and organosiloxanes described by formula



- 20 with the silica hydrogel, where each R<sup>1</sup> is independently selected from a group consisting of hydrocarbon radicals comprising about 1 to 12 carbon atoms and organofunctional hydrocarbon radicals comprising about 1 to 12 carbon atoms, each X is independently selected from a group consisting of halogen and alkoxy radicals comprising about 1 to 12 carbon atoms, a=0, 1, 2, or 3, b=0 or 1, a+b=1, 2, or 3 with the proviso that when b=1 then 25 a+b=2 or 3, and n is an integer of from 2 to 3 inclusive to form a hydrophobic silica hydrogel having a surface area within a range of about 100 m<sup>2</sup>/g to 450 m<sup>2</sup>/g as measured in the dry state.

- The method of the present invention is a three-step procedure, comprising steps (A), (B), and (C) for making hydrophobic silica gels having colloidal silica incorporated therein. 30 Step (A) of the method comprises forming a mixture comprising a preformed silica hydrosol having an average particle size less than 4 nanometers (nm) and a preformed

silica hydrosol having an average particle size of at least 4 nm, referred to herein as "colloidal silica".

Step (B) of the method comprises heating the mixture comprising the silica hydrosol and colloidal silica under strong acid conditions to form a silica hydrogel having the colloidal silica incorporated therein. Step (C) comprises contacting the silica hydrogel prepared in step (B) with an organosilicon compound which reacts with the silica hydrogel to give a hydrophobic silica hydrogel. In a preferred method, sufficient water-immiscible organic solvent is added in step (C) to convert the silica hydrogel or hydrophobic silica hydrogel to the corresponding organogel. The solvent can then be removed from the hydrophobic silica organogel to form a hydrophobic silica gel. Hydrophobic silica gels prepared by the present method have reduced surface area which improves their ease of incorporation into silicone rubber compositions and make them suitable as reinforcing fillers in such compositions.

The method used to prepare the silica hydrosol is not critical and can be any of those known in the art. As used herein the term "silica hydrosols" means those hydrosols of silica having an average particle size less than 4 nanometers (nm). Silica hydrosols useful in the present method can be prepared by, for example, deionizing sodium silicate by a method such as the use of an ion exchange resin. The silica hydrosol may be prepared by hydrolyzing a silane at a low temperature. The silica hydrosol may be prepared by acidifying a sodium silicate mixture.

In the present method, the silica hydrosol provides about 0.02 g to 0.5 g of  $\text{SiO}_2$  per ml of the mixture. Preferably, the silica hydrosol provides about 0.05 g to 0.2 g of  $\text{SiO}_2$  per ml of the mixture.

The mixture of the present method requires the presence of about 0.1 to 50 weight percent of colloidal silica, based on the total weight of the mixture. As used herein the term "colloidal silica" refers to hydrosols of silica having an average particle size of at least 4 nm. Preferred is when the mixture comprises about 10 to 30 weight percent of colloidal silica, based on the total weight of the mixture. Generally, the colloidal silica useful in the present method and compositions can be described as a colloidal amorphous silica that has not at any point existed as a gel during its preparation. The method of preparation of the colloidal silica is not critical to the present method and compositions and can be any of

those known in the art. The colloidal silica can be prepared by, for example, combining an aqueous solution of a soluble metal silicate, such as sodium silicate, and an acid so that the colloidal particles grow in a weakly alkaline solution until the desired particle size is achieved. Preferred is a colloidal silica having an average particle size within a range of 4 to about 300 nm. Even more preferred is a colloidal silica having an average particle size within a range of about 6 to 100 nm.

In step (B), the mixture comprising the silica hydrosol and the colloidal silica must comprise a sufficient concentration of a strong mineral acid such that the pH of the mixture is less than about pH 1. Preferably, there should be a sufficient amount of the strong mineral acid present so that the pH is essentially 0, that is so that the pH cannot be measured. For the purpose of this invention any strong mineral acid can be used. As used herein, the term "strong mineral acid" refers to those acids which ionize to the extent of at least 25 percent in 0.1 N aqueous solution at 18°C. The strong mineral acid may be, for example, hydrochloric, hydroiodic, sulfuric, nitric, and phosphoric acid.

In step (B), the mixture comprising the silica hydrosol and the colloidal silica is heated at a temperature within a range of about 20°C to 250°C. Preferred is when the mixture is heated at a temperature within a range of about 75°C to 150°C. Even more preferred is when, in step (A), the mixture is heated at a temperature within a range of about 90°C to 110°C.

In step (B), the heating time required varies with the temperature and acid concentration. Generally, the higher the temperature and the greater the acid concentration the shorter the heating time needed. The heating of step (B) must be continued until the silica hydrogel having the colloidal silica incorporated therein acquires a structure such that the final product after hydrophobing has a surface area as measured in the dry state within a range of about 100 m<sup>2</sup>/g to 450 m<sup>2</sup>/g as determined by the Brunauer Emmett and Teller (BET) method described in the Jour. Am. Chem. Soc. 60:309 (1938) and as further described in Lentz, U. S. Pat. No. 3,122,520, which is hereby incorporated by reference for such a teaching.

The surface area of the silica hydrogel at the conclusion of step (B) is immaterial provided it is such that the surface area of the dried product after the hydrophobing of step (C) is within the above described range. Generally the surface area of the silica hydrogel is

reduced by the hydrophobing reaction, since the organosilyl groups which become attached to the surface of the silica hydrogel increase the average particle size. The surface of the silica hydrogel can be above  $450 \text{ m}^2/\text{g}$  provided that the hydrophobing treatment brings it within a range of about  $100 \text{ m}^2/\text{g}$  to  $450 \text{ m}^2/\text{g}$ . To determine the proper heating conditions during conduct of step (B) it is necessary to proceed with the hydrophobing of step (C) and then measure the surface area of the resulting product in the dry state. If the surface area of the resulting product in the dry state is above  $450 \text{ m}^2/\text{g}$ , then the acid heating conditions of step (B) were too mild. If the surface area of the resulting product in the dry state is below  $100 \text{ m}^2/\text{g}$ , then the acid heating conditions of step (B) were too severe. Examples of suitable acid concentrations, temperatures, and times for conduct of step (B) are provided in the Examples herein. If the surface area of the hydrophobic silica gel in the dry state is above or below the described range, the hydrophobic silica gels have diminished reinforcing properties in silicone elastomers.

If desired, the silica organogel of step (B) may be subjected to a shearing force to reduce aggregate particle size and to improve the uniformity of the particle size distribution prior to the conduct of the hydrophobing reaction of step (C). The shearing force may be applied to the silica organogel by any of those methods known in the art. The shearing force may be applied, for example, by a mechanical means such as a high-speed mixer or by ultrasound. This reduction in aggregate particle size and improved uniformity of the particle size can provide for hydrophobic silica gels which when compounded into silicone elastomer compositions provide for lower viscosity compositions, more stable compositions, and for cured silicone elastomers having improved clarity and physical properties.

In step (C) of the present method the silica hydrogel of step (B) is contacted with one or more of the defined organosilicon compounds described by formulas (1) and (2) in the presence of a catalytic amount of a strong acid to effect hydrophobing of the silica gel. In step (C), the strong acid can be the same acid which was used in step (B). However, if desired the silica hydrogel can be washed free of acid and a catalytic amount of strong acid added either prior to, simultaneously with, or subsequent to the addition of the organosilicon compound. In the case where the organosilicon compound is, for example, a chlorosilane, the catalytic amount of the strong acid can be generated *in situ* by hydrolysis

of the chlorosilane or the reaction of the chlorosilane directly with hydroxyls of the silica hydrogel. In step (C) the limitations on pH as described for step (B) do not apply. It is only necessary that a catalytic amount of a strong acid be present in an amount sufficient to effect reaction of the organosilicon compound with the silica hydrogel. Examples of useful acids include hydrochloric, sulfuric, and benzene sulfonic acids. It is preferred that in step (C) the strong acid catalyst provide a pH less than about 2.5.

The temperature at which the hydrophobing of step (C) is conducted is not critical and can be from about 20°C to 250°C. Generally it is preferred that the hydrophobing of step (C) be conducted at a temperature within a range of about 30°C to 150°C. The hydrophobing of Step (C) can be conducted at the reflux temperature of the water-immiscible organic solvent when it is present.

In step (C), the silica hydrogel of step (B) is reacted with an organosilicon compound described by formula (1) or (2). In formulas (1) and (2), each  $R^1$  can be independently selected from a group consisting of hydrocarbon radicals comprising about 1 to 12 carbon atoms and organofunctional hydrocarbon radicals comprising about 1 to 12 carbon atoms.  $R^1$  can be a saturated or unsaturated hydrocarbon radical.  $R^1$  can be a substituted or non-substituted hydrocarbon radical.  $R^1$  can be, for example, alkyl radicals such as methyl, ethyl, propyl, t-butyl, hexyl, heptyl, octyl, decyl, and dodecyl; alkenyl radicals such as vinyl, allyl, and hexenyl; substituted alkyl radicals such as chloromethyl, 3,3,3-trifluoropropyl, and 6-chlorohexyl; and aryl radicals such as phenyl, naphthyl, and tolyl.  $R^1$  can be an organofunctional hydrocarbon radical comprising 1 to about 12 carbon atoms where the organic portion of the radical is substituted with reactive atoms or groups such as mercapto, disulfide, polysulfide, amino, carboxylic acid, carbinol, ester, or amido. A preferred organofunctional hydrocarbon radical is one having disulfide or polysulfide functionality.

In formula (1) each X is independently selected from a group consisting of halogen and alkoxy radicals comprising about 1 to 12 carbon atoms. When X is a halogen, it is preferred that the halogen be chlorine. When X is an alkoxy radical, X may be, for example, methoxy, ethoxy, and propoxy. Preferred is where each X is selected from a group consisting of chlorine atoms and methoxy.

The viscosity of the organosiloxanes described by formula (2) is not limiting and can range from that of a fluid to a gum. Generally, higher molecular weight organosiloxanes will be cleaved by the acidic conditions of the present method allowing them to react with the silica hydrogel.

5           The organosilicon compound may be provided to the present method as a single compound as described by formulas (1) or (2) or as a mixture of two or more organosilicon compounds described by formulas (1) and (2).

Examples of useful organosilicon compounds include diethyldichlorosilane, allylmethyldichlorosilane, methylphenyldichlorosilane, phenylethyldiethoxysilane, 3,3,3-  
10   trifluoropropylmethyldichlorosilane, trimethylbutoxysilane, sym-diphenyltetramethyldisiloxane, trivinyltrimethylcyclotrisiloxane, hexaethyldisiloxane, pentylmethyldichlorosilane, divinylpropoxysilane, vinyldimethylchlorosilane, vinylmethyldichlorosilane, vinyldimethylmethoxysilane, trimethylchlorosilane, hexamethyldisiloxane, hexenylmethyldichlorosilane, hexenylmethylchlorosilane,  
15   dimethylchlorosilane, dimethyldichlorosilane, mercaptopropylmethyldimethoxysilane, and bis{3-(triethoxysilyl)propyl}tetrasulfide. When the hydrophobic silica gel is to be used as a filler in silicone rubber, it is preferred that the organosilicon compound be hexamethyldisiloxane or dimethyldichlorosilane.

The amount of organosilicon compound added to the method is that sufficient to  
20   adequately hydrophobe the silica hydrogel to provide a hydrophobic silica gel suitable for its intended use. Generally the organosilicon compound should be added to the method in an amount such that there is at least 0.04 organosilyl unit per  $\text{SiO}_2$  unit in the silica hydrogel, the  $\text{SiO}_2$  units including both those provided by the silica hydrosol and the colloidal silica. The upper limit of the amount of organosilicon compound added to the  
25   process is not critical since any amount in excess of the amount required to saturate the silica gel will act as a solvent for the method.

The hydrophobic silica hydrogel of step (C) may be used as is or may be recovered for use by such methods as centrifugation or filtration. The hydrophobic silica hydrogel may be dried by the use of such methods as heating or reducing pressure or a combination  
30   of both heating and reducing pressure.

In a preferred method a water-immiscible organic solvent in sufficient amount to convert the silica hydrogel or hydrophobic silica hydrogel to the corresponding organogel is added. The organic solvent can be added prior to, simultaneously with, or subsequent to the addition of the organosilicon compound. That is the silica hydrogel can be first converted  
5 into an organogel by replacement of the water with the organic solvent and then hydrophobed. Alternatively, the organosilicon compound and the organic solvent can be added simultaneously to the silica hydrogel. Under these conditions the reaction of the silica hydrogel with the organosilicon compound and the replacement of the water in the hydrophobic silica hydrogel with the organic solvent may occur simultaneously. Finally the  
10 organosilicon compound can be added prior to the organic solvent, in which case the silica hydrogel reacts with the organosilicon compound and the resulting product is then converted into an organogel by an addition of an organic solvent. In the latter two cases the conversion to a silica organogel is accomplished by a phase separation, in which the hydrophobic silica organogel passes into the organic solvent phase. A preferred method is  
15 where a water-immiscible organic solvent is added after formation of the hydrophobic silica hydrogel thereby effecting formation of a hydrophobic silica organogel.

For purpose of this invention any organic solvent immiscible with water can be employed. Suitable water-immiscible solvents include low molecular weight siloxanes such as hexamethyldisiloxane, octamethylcyclotetrasiloxane, diphenyltetramethyldisiloxane  
20 and trimethylsilyl endblocked polydimethylsiloxane fluids. When a siloxane is employed as a solvent it may serve both as a solvent and as a reactant with the silica hydrogel. In addition, suitable solvents include aromatic hydrocarbons such as toluene and xylene; heptane and other aliphatic hydrocarbon solvents; cycloalkanes such as cyclohexane; ethers such as diethylether and dibutylether; halohydrocarbon solvents such as methylene chloride,  
25 chloroform, ethylene chloride, and chlorobenzene; and ketones such as methylisobutylketone.

The amount of water-immiscible organic solvent is not critical so long as there is sufficient solvent to convert the hydrophobic silica hydrogel into a silica organogel. Preferably the solvent should have a boiling point below about 250°C to facilitate its  
30 removal from the hydrophobic silica organogel, however the boiling point is not critical

since the solvent may be removed from the hydrophobic silica organogel by centrifuging or other suitable means.

After the silica hydrogel has been converted to the hydrophobic silica organogel the resulting product may be employed *per se*. That is the hydrophobic silica organogel may be used directly as a reinforcing agent in silicone rubber or in any other uses for which this type of product can be used. Alternatively, the solvent may be removed from the hydrophobic silica organogel and the resulting dry hydrophobic silica gel used.

During the conduct of step (C) it may be desirable to add a surfactant or a water-miscible solvent to facilitate the reaction of the organosilicon compound with the silica hydrogel. The surfactant or water-miscible solvent may be added in the presence or absence of any water-immiscible organic solvent added to the method. Suitable surfactants can include, for example, anionic surfactants such as dodecylbenzene sulfonic acid, nonionic surfactants such as polyoxyethylene(23)lauryl ether and  $(\text{Me}_3\text{SiO})_2\text{MeSi}(\text{CH}_2)_3(\text{OCH}_2\text{CH}_2)_7\text{OMe}$  where Me is methyl, and cationic surfactants such as N-alkyltrimethyl ammonium chloride. Suitable water-miscible solvents can include, for example, alcohols such as ethanol, propanol, isopropanol, n-butanol, and tetrahydrofuran.

In step (C) of the present method an effective amount of a heat stabilizing agent selected from a group consisting of water soluble compounds of cerium and iron may be added. By the term "effective amount" it is meant that the water soluble compound of cerium or iron is present in the hydrophobic silica gel at a concentration sufficient to provide improved heat stability to those compositions in which the hydrophobic silica gel is incorporated. Such compositions can include, for example, silicone rubber, natural rubber, and synthetic organic rubber.

Generally, about 0.01 percent weight/volume (% Wt./Vol.) to 10 %Wt./Vol. of the water soluble compound of cerium or iron in relation to the volume of components in step (C), excluding solvents, is considered useful in the present process. Preferred is where the water soluble compound of cerium or iron comprises about 0.1 %Wt./Vol. to 1 %Wt./Vol. on the same basis.

Examples of water soluble compounds which may be useful in the present method include  $\text{FeCl}_3$ ,  $\text{FeBr}_2$ ,  $\text{FeBr}_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ ,  $\text{FeI}_2 \cdot 4\text{H}_2\text{O}$ ,  $\text{Fe}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ ,  $\text{CeCl}_3 \cdot 9\text{H}_2\text{O}$ ,  $\text{CeBr}_3 \cdot \text{H}_2\text{O}$ ,  $\text{CeI}_3 \cdot 9\text{H}_2\text{O}$ ,  $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ , and  $\text{Ce}(\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$ . A preferred

water soluble compound of cerium or iron for use in the present method is selected from the group consisting of  $\text{FeCl}_3$  and  $\text{CeCl}_3 \cdot 9\text{H}_2\text{O}$ .

The following examples are provided to illustrate the present invention. These examples are not intended to limit the scope of the present claims.

5           Example 1. A silica gel having incorporated therein colloidal silica was hydrophobed with hexamethyldisiloxane. 750 ml of PQ N Clear Sodium Silicate (PQ Corporation, Valley Forge, PA) was diluted with 1350 ml of deionized water. This solution was added at a rate of 420 ml per minute to a rapidly stirred solution comprising 280 ml of concentrated hydrochloric acid (HCl) (Fisher Certified, Fisher Scientific, Fair Lawn, NJ)  
10       diluted with 620 ml of deionized water. The resulting mixture was stirred for 2 minutes and then the pH adjusted to 2.5 using a sodium silicate solution. The resulting 3100 ml of silica hydrosol contained 0.1 g of  $\text{SiO}_2$  per milliliter.

          The silica hydrosol prepared as described above was deionized by pumping through a 1.5 m x 5 cm column packed with 1500 ml of Dowex 50WX8-100 ion exchange resin in  
15       the acid form (The Dow Chemical Company, Midland, MI) at a rate of 60 ml per minute. The pH of the column effluent was monitored until the pH dropped below 0.5, at which point the next 2000-2400 ml of deionized silica hydrosol effluent was collected.

          The deionized silica hydrosol was agglomerated by placing 1 L of the deionized silica hydrosol in a 5 L flask and, while stirring, adding 273 ml of colloidal silica (Ludox®  
20       SM, DuPont Chemicals, Wilmington, DE, average particle size of 10 nm) and 392 ml of concentrated HCl (Fisher Certified). The silica hydrogel which formed within a few minutes of addition of the HCl was broken-up by additional stirring to form a suspension comprising an agglomerated silica hydrogel having incorporated therein the colloidal silica. The silica hydrogel suspension was heat treated at 100°C for 3 hours and then cooled to  
25       room temperature.

          The heat-treated silica hydrogel suspension was hydrophobed as follows. To the heat-treated silica hydrogel suspension, with stirring, was added 555 ml of isopropanol followed by 288 ml of hexamethyldisiloxane. The resulting mixture was stirred for 1 hour at room temperature. Then, 1 L of toluene was added to the mixture. This mixture was  
30       mildly stirred for an additional 5 minutes, stirring stopped, and the aqueous phase drained from the bottom of the flask. The toluene phase was washed with 500 ml of deionized

water. The flask was then fitted with a Dean-Stark trap and the toluene phase refluxed to remove residual water. The toluene phase was removed by distillation under reduced pressure leaving as product a hydrophobic silica gel. The hydrophobic silica gel was dried overnight at 150°C to remove residual toluene. The yield of hydrophobic silica gel was 202

5 g. Example 2. A silica gel having incorporated therein colloidal silica was hydrophobed with hexamethyldisiloxane. A deionized silica hydrosol was prepared as described in Example 1. The deionized silica hydrosol was agglomerated by placing 1 L of the deionized silica hydrosol in a 5 L flask and, while stirring, adding 216 ml of colloidal silica (Nalco® 1050, Nalco Chemical Co., Chicago, IL) and 375 ml of concentrated HCl  
10 (Fisher Certified). The silica hydrogel which formed within a few minutes of addition of the HCl was broken-up by additional stirring to form a suspension comprising an agglomerated silica hydrogel having incorporated therein the precipitated silica. The silica hydrogel suspension was heat treated by refluxing for 3 hours and then cooled to room temperature.

15 The heat-treated silica hydrogel suspension was hydrophobed as follows. To the heat-treated silica hydrogel suspension, with stirring, was added 530 ml of isopropanol followed by 100 ml of hexamethyldisiloxane. The resulting mixture was stirred for 1 hour at room temperature. Then, 1.3 L of toluene were added to the mixture. This mixture was mildly stirred for an additional 5 minutes, stirring stopped, and the aqueous phase drained  
20 from the bottom of the flask. The toluene phase was washed with 500 ml of deionized water. The flask was then fitted with a Dean-Stark trap and the toluene phase refluxed to remove residual water. The toluene phase was transferred to an open container in an exhaust hood and the toluene allowed to evaporate leaving as product a hydrophobic silica gel. The hydrophobic silica gel was dried for 4 hours at 150°C to remove residual toluene.  
25 The yield of dried hydrophobic silica gel was 267 g. The BET surface area of the dried hydrophobic silica gel was determined by the method described supra, and the result is reported in Table 1.

Example 3. A silica gel having incorporated therein colloidal silica was hydrophobed with hexamethyldisiloxane. A deionized silica hydrosol was prepared as  
30 described in Example 1. The deionized silica hydrosol was agglomerated by placing 1 L of the deionized silica hydrosol in a 5 L flask and, while stirring, adding about 130 ml of

colloidal silica (Nalco® 1140, Nalco Chemical Co.) and 375 ml of concentrated HCl (Fisher Certified). The silica hydrogel which formed within a few minutes of addition of the HCl was broken-up by additional stirring to form a suspension comprising an agglomerated silica hydrogel having incorporated therein the colloidal silica. The silica hydrogel suspension was heat treated by refluxing for 3 hours and then cooled to room temperature.

The heat-treated silica hydrogel suspension was hydrophobed as follows. To the heat-treated silica hydrogel suspension, with stirring was added 530 ml of isopropanol followed by 100 ml of hexamethyldisiloxane. The resulting mixture was stirred for 1 hour at room temperature. Then, 1750 ml of toluene were added to the mixture. This mixture was stirred for an additional 5 minutes, stirring stopped, and the aqueous phase drained from the bottom of the flask. The toluene phase was washed with 500 ml of deionized water. The flask was fitted with a Dean-Stark trap and the toluene phase refluxed to remove residual water. The toluene phase was transferred to an open container in an exhaust hood and the toluene allowed to evaporated leaving as product a hydrophobic silica gel. The hydrophobic silica gel was dried for 4 hours at 150°C to remove residual toluene. The yield of dried hydrophobic silica gel was 186 g. The BET surface area of the dried hydrophobic silica gel was determined by the method described in Example 2 and the result is reported in Table 1.

Example 4. A silica gel having incorporated therein colloidal silica, hydrophobed with hexamethyldisiloxane, and heat stabilized by the addition of FeCl<sub>3</sub> was prepared. 400 ml of PQ N Clear Sodium Silicate (PQ Corporation) was diluted with 600 ml of deionized water. This solution was added at a rate of 375 ml per minute to a stirred solution comprising 440 ml of concentrated HCl (Fisher Certified) diluted with 560 ml of deionized water to form a silica hydrosol comprising 0.08 g SiO<sub>2</sub>/ml. Immediately after completion of the addition of the sodium silicate to the HCl solution, 309 ml of Ludox® HS (DuPont Chemicals) was added with continuous stirring. The resulting 2 L of silica hydrosol was filtered through a fritted glass filter funnel and the silica hydrosol poured into pans. The silica hydrosol gelled in approximately 35 minutes and was let set for an hour after gelation. The resulting silica hydrogel was cut into approximately 1 cm squares and washed with deionized water until the pH of the effluent was about pH 2.1. The washed silica hydrogel

was placed in a 5 L flask, 839 ml of concentrated HCl (Fisher Certified) added, and the resulting mixture heated to reflux for 5 hours. The refluxed silica hydrogel was cooled to room temperature.

5 The heat-treated silica hydrogel suspension was hydrophobed as follows. To the silica hydrogel, with stirring, was added 1049 ml of isopropanol, 543 ml of hexamethyldisiloxane and 8.3 g of  $\text{FeCl}_3$ . After stirring the flask content 1 hour at room temperature, 2 L of toluene were added. After mild stirring the flask content for an additional 5 minutes, stirring was stopped and the aqueous bottom phase drained from the flask. The toluene phase was washed with 500 ml of deionized water. The flask was fitted  
10 with a Dean-Stark trap and the toluene phase refluxed to remove residual water. After refluxing the toluene was removed by distillation under reduced pressure leaving as product a hydrophobic silica gel. The hydrophobic silica gel was dried overnight at  $150^\circ\text{C}$ . The yield of dried hydrophobic silica gel was 299 g. The BET surface area was determined by the method described in Example 2. The carbon and hydrogen content of the dried  
15 hydrophobic silica gel was determined by CHN analysis using a Perkin Elmer Model 2400 CHN Elemental Analyzer (Perkin Elmer Corporation, Norwalk, CT). The iron content of the dried hydrophobic silica gel was determined by atomic adsorption. The results of these analysis are reported in Table 1.

Example 5. A silica gel having incorporated therein colloidal silica, hydrophobed  
20 with hexamethyldisiloxane, and heat stabilized by the addition of  $\text{FeCl}_3$  was prepared. A silica hydrosol comprising about 0.1 g of  $\text{SiO}_2/\text{ml}$  was prepared and deionized as described in Example 1. One liter of the deionized silica hydrosol was placed in a 5 L flask and while stirring 273 ml of Ludox® SM (DuPont Chemicals) were added, followed by 392 ml of concentrated HCl. The silica hydrogel which formed within a few minutes of addition of  
25 the HCl was broken-up by additional stirring to form a silica hydrogel suspension. The silica hydrogel suspension was heat-treated at  $100^\circ\text{C}$  for 3 hours and then cooled to room temperature.

The heat-treated silica hydrogel was hydrophobed as follows. To the heat-treated silica hydrogel, with stirring, was added 555 ml of isopropanol, 288 ml of  
30 hexamethyldisiloxane, and 2.7 g of  $\text{FeCl}_3$ . The resulting mixture was stirred for 1 hour at room temperature and then 1 L of toluene was added to the mixture. This mixture was

mildly stirred for an additional 5 minutes, then stirring stopped and the aqueous phase drained from the bottom of the flask. The toluene phase was washed with 500 ml of deionized water. The flask was fitted with a Dean-Stark trap and the toluene phase refluxed to remove residual water. The toluene phase was distilled under reduced pressure leaving as product a hydrophobic silica gel. The hydrophobic silica gel was dried overnight at 150°C to remove residual toluene. The yield of dried hydrophobic silica gel was 210 g. The dried hydrophobic silica gel was analyzed to determine surface area, carbon and hydrogen content, and iron content by the methods described in Example 4. The results of this analysis are reported in Table 1.

Example 6. A silica gel having incorporated therein colloidal silica, hydrophobed with hexamethyldisiloxane and vinyltrimethylchlorosilane, and heat stabilized by the addition of FeCl<sub>3</sub> was prepared. A deionized silica hydrosol was prepared as described in Example 1. The deionized silica hydrosol was agglomerated by placing 1 L of the deionized silica hydrosol in a 5 L flask and while stirring adding 273 ml of colloidal silica (Ludox® SM, DuPont Chemicals) and 392 ml of concentrated HCl (Fisher Certified). The mixture was heat-treated by refluxing for 3 hours with stirring to form a suspension comprising a silica hydrogel having incorporated therein the colloidal silica. The resulting heat-treated silica hydrogel was cooled to room temperature.

The heat-treated silica hydrogel was hydrophobed as follows. To the heat-treated silica hydrogel, with stirring, was added 555 ml of isopropanol, 78 ml of hexamethyldisiloxane, and 2.7 g of FeCl<sub>3</sub>. The resulting mixture was stirred for 1 hour at room temperature. Then, 2 L of toluene were added to the mixture. This mixture was stirred for several minutes, stirring stopped, and the aqueous phase drained from the bottom of the flask. The toluene phase was washed with 1 L of deionized water. The treatment flask was then fitted with a Dean-Stark trap and the toluene phase refluxed to remove residual water. The toluene phase was heated at 110°C to remove residual hexamethyldisiloxane and then 5 ml of vinyltrimethylchlorosilane were added. This mixture was refluxed for 1 hour and cooled to room temperature. About 50 ml of deionized water were added to the flask to washout residual HCl and the toluene phase refluxed to remove residual water. The toluene phase was transferred to an open container in an exhaust hood and the toluene allowed to evaporate leaving as product a hydrophobic silica

gel. The hydrophobic silica gel was dried overnight at 85°C. The yield of dried hydrophobic silica gel was 214 g. Selected physical parameters of the dried hydrophobic silica gel were characterized by standard methods and the results are reported in Table 2.

5           Example 7. A silica gel having incorporated therein colloidal silica, hydrophobed with hexamethyldisiloxane and vinyltrimethylchlorosilane, and heat stabilized by the addition of FeCl<sub>3</sub> was prepared. The silica hydrogel was sheared prior to hydrophobing to reduce aggregate particle size and to improve the uniformity of the particle size distribution.

A deionized silica hydrosol was prepared by a method similar to that described in Example

10   1. The deionized silica hydrosol was agglomerated by placing 1 L of the deionized silica hydrosol in a 5 L flask and while stirring adding 273 ml of colloidal silica (Ludox® SM, DuPont Chemicals) and 392 ml of concentrated HCl (Fisher Certified). The mixture was heat treated by refluxing for 3 hours with stirring to form a suspension comprising an silica hydrogel having incorporated therein the colloidal silica.

15   After cooling to room temperature the silica hydrogel was sheared in a Waring Blender (Model 7011, Waring Products Division of Dynamics Corporation of America, New Hartford, CT) for 2 minutes and then returned to the 5 L flask.

The heat-treated and sheared silica hydrogel was hydrophobed as follows. To the silica hydrogel, with stirring, was added 555 ml of isopropanol, 117 ml of

20   hexamethyldisiloxane, and 2.7 g of FeCl<sub>3</sub>. The resulting mixture was stirred for 1 hour at room temperature. Then, 2 L of toluene were added to the mixture. This mixture was mildly stirred for several minutes, stirring stopped, and the aqueous phase drained from the bottom of the flask. The toluene phase was washed with 1 L of deionized water. The flask was then fitted with a Dean-Stark trap and the toluene phase refluxed to remove residual

25   water. The toluene phase was heated at 110°C to remove residual hexamethyldisiloxane and then 5 ml of vinyltrimethylchlorosilane were added to the flask. This mixture was refluxed for 1 hour and cooled to room temperature. About 50 ml of deionized water were added to the flask to washout residual HCl and the toluene phase refluxed to remove

30   residual water. The toluene phase was transferred to an open container in an exhaust hood and the toluene allowed to evaporate leaving as product a hydrophobic silica gel. The hydrophobic silica gel was dried overnight at 85°C. The yield of dried hydrophobic silica

gel was 209 g. Selected physical parameters of the dried hydrophobic silica gel were characterized by standard methods and the results are reported in Table 2.

Example 8. A silica gel having incorporated therein colloidal silica, hydrophobed with hexamethyldisiloxane and vinyltrimethylchlorosilane, and heat stabilized by the addition of  $\text{FeCl}_3$  was prepared. The silica hydrogel was sheared prior to hydrophobing to reduce aggregate particle size and to improve the uniformity of the particle size distribution.

A deionized silica hydrosol was prepared by a method similar to that described in Example 1. The deionized silica hydrosol was agglomerated by placing 1.5 L of the deionized silica hydrosol in a 5 L flask and while stirring adding 409.5 ml of colloidal silica (Ludox® SM, DuPont Chemicals) and 588 ml of concentrated HCl (Fisher Certified). The mixture was heat treated by refluxing for 3 hours with stirring to form a suspension comprising a silica hydrogel having incorporated therein the colloidal silica.

After cooling to room temperature, the silica hydrogel was sheared in a Waring Blender (Model 7011) for 2 minutes and then returned to the 5 L flask.

The heat-treated and sheared silica hydrogel suspension was hydrophobed as follows. To the silica hydrogel suspension, with stirring, was added 832.5 ml of isopropanol, 175 ml of hexamethyldisiloxane, and 4 g of  $\text{FeCl}_3$ . The resulting mixture was stirred for 1 hour at room temperature. Then, 3.2 L of toluene were added to the mixture. This mixture was mildly stirred for several minutes, stirring stopped, and the aqueous phase drained from the bottom of the flask. The toluene phase was washed with 1 L of deionized water. The flask was then fitted with a Dean-Stark trap and the toluene phase refluxed to remove residual water. The toluene phase was heated at  $110^\circ\text{C}$  to remove residual hexamethyldisiloxane and then 3.75 ml of vinyltrimethylchlorosilane were added to the flask. This mixture was refluxed for 1 hour and then cooled to room temperature. About 50 ml of deionized water were added to the flask to washout residual HCl and the toluene phase refluxed to remove residual water. The toluene phase was transferred to an open container in an exhaust hood and the toluene allowed to evaporate leaving as product a hydrophobic silica gel. The hydrophobic silica gel was dried overnight at  $85^\circ\text{C}$ . The yield of dried hydrophobic silica gel was 292 g. Selected physical parameters of the dried hydrophobic silica gel were characterized by standard methods and the results are reported in Table 2.

Example 9. Each of the dried hydrophobic silica gels prepared in Examples 1 through 5 were compounded into a liquid silicone rubber composition, the composition cured, and the physical properties determined. Each of the dried hydrophobic silica gels was compounded at 38 parts per hundred (pph) by weight into a polydimethylsiloxane gum containing about 0.15 mole percent vinyl radicals substituted on silicon atoms and having a plasticity of about 55 to 65. Into this base composition was blended 0.7 pph by weight of 2,5-bis(tert-butylperoxy)-2,5-dimethylhexane, based on the weight of the polydimethylsiloxane gum. The catalyzed base composition was cured in appropriate configurations for physical property testing by hot pressing at 34.5 MPa for 15 minutes at 175°C. The following test methods were used to test the cured silicone rubber: Tensile, ASTM D412; Elongation, ASTM D412; 100% Modulus, ASTM D412; 50% Modulus, ASTM D412; Durometer (Shore A), ASTM 2240; Tear (Die B), ASTM D624; Tear (Die C), ASTM D624; Compression set (22 h at 177°C), ASTM D395. Plasticities of the uncured compositions were measured on samples weighing two times the specific gravity of the composition that were formed into balls and rested one hour before measurement by ASTM 926. The results of this testing are provided in Table 1.

Example 10. Each of the dried hydrophobic silica gels prepared in Examples 6 through 8 were compounded into a silicone rubber composition, the composition cured, and the physical properties determined. Each of the dried hydrophobic silica gels was compounded at the parts per hundred (pph) by weight described in Table 2 into a siloxane mixture. The temperature at which this compounding was effected is also provided in Table 2. The siloxane mixture comprised 83.8 weight percent vinyl dimethylsiloxyl end-blocked polydimethylsiloxane having a viscosity of 55 Paxes at 25°C and 16.2 weight percent of a vinyl dimethylsiloxyl end-blocked poly(vinylmethyl)dimethylsiloxane copolymer having 2 mole percent vinyl substitution on silicon and a viscosity of 0.35 Paxes at 25°C. Into this base composition was blended a cure system comprising a low-molecular weight polydimethyl(methylhydrogen)siloxane fluid, neutralized complex of platinum dichloride with sym-divinyltetramethyldisiloxane, and 1-ethynyl-cyclohexanol. The

catalyzed base composition was cured in appropriate configurations for physical property testing by hot pressing at 34.5 MPa for 10 minutes at 150°C. The cured compositions were post-cured for 1 hour at 177°C. Physical properties of the cured compositions were determined by test methods described in Example 9 and the results are reported in Table 2.

5

Table 1  
Physical Properties of Silicone Rubber Reinforced  
With Hydrophobic Silica Gels

Property	Example Number				
	1	2	3	4	5
BET Surface Area (m <sup>2</sup> /g)	-	268	361	342	355
Wt. % Carbon	-	-	-	6.3	6.0
Wt. % Hydrogen	-	-	-	1.5	1.5
Wt. % Iron	-	-	-	0.45	0.43
Plasticity	142	-	-	101	113
Tensile (MPa)	7.76	4.68	6.55	6.69	7.12
Elongation (%)	815	690	785	1291	824
Modulus @ 50% (MPa)	0.61	0.52	0.65	0.31	0.54
Modulus @ 100% (MPa)	0.89	0.73	0.89	0.49	0.80
Durometer (Shore A)	50	-	-	39	46
Tear B (kN/m)	12.43	7.84	11.56	10.50	11.60
Tear C (kN/m)	14.53	11.41	13.85	11.20	13.23
Comp. Set (% @ 22h)	-	-	-	11	15

\*-Indicates data not available

Table 2  
Physical Properties of Silicone Rubber Reinforced  
With Hydrophobic Silica Gels

Property	Example Number					
	6	7			8	
BET Surface Area (m <sup>2</sup> /g)	357	357			372	
Void Volume (cm <sup>3</sup> /g)	4.56	4.60			4.23	
Pore Volume (cm <sup>3</sup> /g)	2.49	2.47			2.37	
Ave. Pore Dia. (angstrom)	173	167			164	
Ave. Particle Size (μm)	36.6	34.8			33.3	
Mixing Temp. (°C)	R.T.*	100	60	60	60	60
Parts Silica Gel	30	30	35	40	30	40
Tensile (MPa)	4.71	6.01	6.11	6.58	6.14	7.20
Elongation (%)	217	364	458	410	368	472
Modulus @ 100% (MPa)	2.97	2.38	2.59	2.75	2.08	2.45
Durometer (Shore A)	58	54	59	62	48	57
Tear Die B (kN/m)	37.1	38.2	44.5	39.9	38.9	42.5

\* Room Temperature

We claim:

1. A method for preparing a hydrophobic silica gel comprising:

(A) forming a mixture comprising (i) a silica hydrosol comprising about 0.02 g to 0.5 g of SiO<sub>2</sub> per milliliter and having an average particle size less than 4 nm and (ii) 0.1 to 50 weight percent of colloidal silica having an average particle size of at least 4 nm,

(B) heating the mixture in the presence of a strong mineral acid at a pH less than about pH 1 and a temperature within a range of about 20°C to 250°C to form a silica hydrogel having the colloidal silica incorporated therein, and

(C) mixing the silica hydrogel with (1) a catalytic amount of a strong acid in an amount sufficient to effect reaction of (2) an organosilicon compound selected from the group consisting of organosilanes described by formula



and organosiloxanes described by formula



with the silica hydrogel, where each R<sup>1</sup> is independently selected from a group consisting of hydrocarbon radicals comprising about 1 to 12 carbon atoms and organofunctional hydrocarbon radicals comprising about 1 to 12 carbon atoms, each X is independently selected from a group consisting of halogen and alkoxy radicals comprising 1 to 12 carbon atoms, a=0, 1, 2, or 3, b=0 or 1, a+b=1, 2, or 3 with the proviso that when b=1 then a+b=2 or 3, n is an integer of from 2 to 3 inclusive to form a hydrophobic silica hydrogel having a surface area within a range of about 100 m<sup>2</sup>/g to 450 m<sup>2</sup>/g as measured in the dry state.

2. A method according to Claim 1, where the mixture comprises about 0.05 g to 0.2 g of SiO<sub>2</sub> per milliliter.

3. A method according to Claim 1, where the mixture comprises about 10 to 30 weight percent of colloidal silica.

4. A method according to Claim 1, where the colloidal silica has a particle size within a range of about 6 to 100 nm.

5 5. A method according to Claim 1, where the mixture is heated at essentially pH 0.

6. A method according to Claim 1, where the mixture is heated at a temperature within a range of about 75°C to 150°C and essentially pH 0.

10

7. A method according to Claim 1 further comprising shearing the silica hydrogel of step (B) prior to conduct of step (C).

8. A method according to Claim 1, where during the contacting of step (C) the strong acid provides for a pH less than about pH 2.5.

15

9. A method according to Claim 1, where the contacting of step (C) is effected at a temperature within a range of about 20°C to 250°C.

10. A method according to Claim 1, where the contacting of step (C) is effected at a temperature within a range of about 30°C to 150°C.

20

11. A method according to Claim 1, where the organosilicon compound is an organosilane.

25

12. A method according to Claim 11, where the organosilane is selected from the group consisting of vinyl dimethylchlorosilane, hexenylmethylchlorosilane, hexenyl dimethylchlorosilane, and dimethyldichlorosilane.

30

13. A method according to Claim 1, where the organosilicon compound is an organosiloxane.

14. A method according to Claim 13, where the organosiloxane is hexamethyldisiloxane.

15. A method according to Claim 1, where the organosilicon compound provides at least 0.04 organosilyl units per  $\text{SiO}_2$  unit of the silica hydrogel.

16. A method according to Claim 1 further comprising contacting the hydrophobic silica hydrogel with a water-immiscible organic solvent in sufficient amount to convert the hydrophobic silica hydrogel to a hydrophobic silica organogel.

17. A method according to Claim 1 further comprising during the contacting of step (C) the presence of a surfactant which facilitates reaction of the organosilicon compound with the silica hydrogel.

18. A method according to Claim 1 further comprising during the contacting of step (C) the presence of a water-miscible solvent which facilitates reaction of the organosilicon compound with the silica hydrogel.

19. A method according to Claim 1 further comprising contacting the silica hydrogel with an effective amount of a heat stabilizing agent selected from the group consisting of water soluble compounds of cerium and iron.

20. A method according to Claim 19, where the water soluble compounds of cerium and iron are selected from the group consisting of  $\text{FeCl}_3$  and  $\text{CeCl}_3 \cdot 9\text{H}_2\text{O}$ .

21. A composition prepared by the method of Claim 1.

22. A composition prepared by the method of Claim 7.

23. A composition prepared by the method of Claim 16.

5

24. A composition prepared by the method of Claim 19.

## INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 98/03273

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 6 C01B33/16 C09C1/30

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 6 C01B C09C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 3 122 520 A (CHARLES W. LENTZ) 25 February 1964 cited in the application see the whole document ---	1,5,6, 8-14,16, 18,21-24
A	EP 0 653 378 A (ENIRICERCH SPA ; ENICHEM SPA (IT)) 17 May 1995 see claims 1-7 see page 3, line 51 - page 6, line 26 see examples 16-19,24-26 ---	1-4
P, A	US 5 708 069 A (BURNS GARY THOMAS ET AL) 13 January 1998 see the whole document ---	1,19,20
-/--		

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

## \* Special categories of cited documents:

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## INTERNATIONAL SEARCH REPORT

Internal Application No

PCT/US 98/03273

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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